

AU 0253031

JUL 1964

H OF AUSTRALIA

5283/61

## PATENT SPECIFICATION

Complete Specification Lodged ..... 31st May, 1961.

Application Lodged (No. 5283/61) ..... 31st May, 1961.

AUSTRALIA

DIV 130

Applicant ..... Harburger Fettchemie Brinckman &amp; Mergell GmbH.

Actual Inventors ..... Dr. Josef Baltes, Dr. Friedrich Weghorst and Otto Wechmann.

Complete Specification Published ..... 2nd May, 1963.

Complete Specification Accepted ..... 15th July, 1964.

Classification 09.1.

International Classification C 07 c.

No drawing.

## COMPLETE SPECIFICATION.

PROCESS FOR CATALYTIC ISOMERISATION OF COMPOUNDS OF UNCONJUGATED  
POLYETHENOID ACIDS.

The following statement is a full description of this invention, including the best method of performing it known to us:-

The invention relates to a process for a substantially complete catalytic conversion of compounds of unconjugated polyethenoid acids into compounds of conjugated ethenoid acids.

It is known that certain properties of unsaturated fatty acids and their derivatives can be altered by rearrangement of the structure of the double bond, either with respect to their steric position or their position in the carbon chain of the molecule of the fatty acid. This reaction is named "isomerisation". Unsaturated fatty acids having more than one  $-\text{CH}=\text{CH}-$  group in the chain are also known as "polyethenoid acids"; molecules with such contiguous groups having double bond between two carbon atoms such as  $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$  are known as conjugated ethenoid acids, while non-contiguous groups of this configuration will be considered as unconjugated ethenoid acids. The latter ones, namely the unconjugated polyethenoid acids occur in nature in large quantities, while conjugated polyethenoid acids are relatively seldom found in fats or oils of natural origin except for wood oils such as tung oil. The latter compound and also its derivatives are of great technical interest and, therefore, many attempts were made to isomerise unconjugated polyethenoid acids to conjugated ones. Theoretically, such a shifting of the double bond is possible because the conjugated form has a lower state of energy than the unconjugated form.

Because of the fact that conjugated unsaturated compounds are obtained by hydrogenation of fats, catalysts, similar to those used for hydrogenation, have been used for isomerisation, especially nickel catalysts. However, when using such catalysts, an incomplete isomerisation is achieved, and also unwanted side reactions occur; these side reactions, especially polymerisation and intramolecular cyclisation take place to a more or less large extent.

The known isomerisation with an excess of alkali metal hydroxide in an aqueous or alcoholic medium leads to a quantitative isomerisation. This reaction is also used for a quantitative determination of, unconjugated polyethenoid acids, because the conjugated polyethenoid acids formed by the isomerisation of the unconjugated acids may be determined and measured by spectrophotometric methods. Not only on a technical scale but also in the analytical method a considerable excess of alkali metal hydroxide must be used, so that the conjugated fatty acids or fatty acid compounds are obtained in form of their alkali soaps and have to be recovered and isolated accordingly. These techniques differ in the use of a particular solvent, temperature and pressure.

Catalysts which may be used for this so-called alkali isomerisation at first react, under conditions applied so far, in stoichiometrical amounts or proportions with the functional groups of the fatty acids or their compounds such as carboxyl groups, ester groups, amide groups, and similar groups before an isomerisation can be obtained. Thereby, a corresponding amount of the catalyst is inactivated and the isomerisation can be achieved only by addition of an excessive amount of catalyst.

The conditions of reaction in the analytical method involve several disadvantages, and in consequence potassium tertiary-butyrate in tertiary-butanol is sometimes used as isomerisation agent. In that case the isomerisation can be carried out at a temperature of about 85°C within a period of about 4 hours, although higher temperatures up to 140°C are possible, a larger amount than the stoichiometric amount of potassium tertiary butyrate always being used.

Surprisingly it has now been found that the quantitative catalytic isomerisation to conjugated polyethenoid compounds of monohydric alcohol esters, amides and polyamides of unconjugated polyethenoid acids can be effected by a process which is characterised in that the unconjugated polyethenoid compound is treated with catalytic amounts of 0.5 to 5% and preferably with 0.3 to 2%, by weight of alkali metal alcoholate, especially from monohydric alcohols, at a temperature between 60 and 180°C. and preferably between 100 and 140°C. in the absence of compounds which will react with the alkali metal alcoholate to inactivate it, and in particular water, free fatty acids, or peroxides. The isomerisation may also be carried out in the presence of alcohols or of polar or nonpolar solvents which are inert with respect to the catalyst, for example, heptane, dimethyl formamide and dimethyl sulphoxide. Volatile compounds used as solvents may be removed by distillation during the isomerisation.

Conveniently the starting materials may be mixtures of monohydric alcohol esters, amides and polyamides of the unconjugated polyethenoid acids or fatty mixtures containing these compounds.

The method according to the invention has the main advantage that isomerisation is possible using less than stoichiometrical amounts of alkali metal alcoholates avoiding thereby the serious disadvantages connected therewith.

The catalysts used in connection herewith belong to the group of interesterification or ester exchange catalysts, i. e. catalysts which can accelerate both the

interesterification and isomerisation reactions. Their effectiveness decreases according to the following order: caesium, rubidium, potassium, sodium, lithium, magnesium, zinc. Potassium alcoholates are especially useful as isomerisation catalysts for technical purposes not only because of their adequate catalytic activity but also for their partially associated solubility.

Alkali metal compounds of any monohydric alcohol can be used as catalyst, for example, alkali metal compounds of methyl alcohol, ethyl alcohol, propyl alcohol, or butyl alcohol. Potassium methylate is preferred. Alkali metals, alkali metal hydrides and organic alkali metal compounds e.g. alkali metal amides, may be used so long as they are capable of reacting with any alcohol present in the reaction mixture to give corresponding alkali metal alcoholates. According to the invention as stated above the catalyst is used in the amount of 0.05-5% by weight and preferably of 0.3-2%, based on the amount of the polyethenoid acid compound to be isomerised.

The activity of the above mentioned catalysts can be increased remarkably by adding small amounts of all kinds of monohydric alcohols. Particularly suitable catalyst mixtures of this type are mixtures of alkali metal alcoholates with a monohydric alcohol in the proportion of one mole of alkali metal alcoholate per 0.1-5.0 moles, and preferably 0.5-2.0 moles of alcohol, or solutions of the alkali metal alcoholate in the said alcohols.

The temperature of treatment has an important influence on the rate of the reaction and also on the occurrence of undesired side reactions. A sufficient rate of isomerisation for practical purposes is only observed at temperatures above 60°C while above a temperature of 140°C side reactions may be observed to a noticeable extent. The best range of temperature is between 100 and 140°C.

For this isomerisation reaction all esters of unconjugated polyethenoid acids with monohydric alcohols, especially those of the naturally occurring linoleic acid, linolenic acid and arachidonic acid and also of the higher polyethenoid acids of marine-animal origin namely tri-, tetra-, penta- and hexethenoid acids may be used, furthermore any amides of the abovementioned fatty acids and polyamides of these fatty acids, the functional groups of which are incapable of an inactivating reaction with the catalyst may also be used. According to the invention the isomerisation reaction can be controlled in such a way that a partial conjugation of diene acids and more highly unsaturated fatty acids is favoured.

The isomerisation of the unconjugated polyethenoid fatty acid esters can be carried out so that interesterification takes place at the same time and if an amine is present aminolysis will also be carried out simultaneously with isomerisation.

To control the progress of isomerisation, a test is used as described by B. Sreenivasan and J. B. Brown in Journal of the American Oil Chemists Society, volume 33 page 521 (1956) and volume 35 page 89 (1958). According to this method the original substrata, the final product and also samples of the reaction mixture withdrawn at certain time intervals are analysed. The extent of the isomerisation is given by the measured  $E_{1\text{cm}}^{1\%}$  values in relation to the  $E_{1\text{cm}}^{1\%}$  determined by the above method. The extent of isomerisation of diethenoid acids is given by

$$\frac{E_{1\text{cm}}^{1\%} \text{ at } 234 \text{ m}\mu \text{ determined} - (E_{1\text{cm}}^{1\%} \text{ at } 268 \text{ m}\mu \text{ determined} \times \frac{631}{742})}{E_{1\text{cm}}^{1\%} \text{ at } 234 \text{ m}\mu \text{ analytical} - (E_{1\text{cm}}^{1\%} \text{ at } 268 \text{ m}\mu \text{ analytical} \times \frac{631}{742})} \times 100$$

$$\frac{E_{1\text{cm}}^{1\%} \text{ at } 234 \text{ m}\mu \text{ analytical} - (E_{1\text{cm}}^{1\%} \text{ at } 268 \text{ m}\mu \text{ analytical} \times \frac{631}{742})}{E_{1\text{cm}}^{1\%} \text{ at } 234 \text{ m}\mu \text{ determined} - (E_{1\text{cm}}^{1\%} \text{ at } 268 \text{ m}\mu \text{ determined} \times \frac{631}{742})} \times 100$$

and the extent of isomerisation of the triethenoid acids is given by

$$\frac{\text{determined } E_{1\text{cm}}^{1\% \text{ at } 268 \text{ m } \mu}}{\text{analytical } E_{1\text{cm}}^{1\% \text{ at } 268 \text{ m } \mu}} \times 100$$

In this it is assumed that the method of Sreenivasan and Brown results in complete isomerisation.

In the examples the percentage isomerisation is calculated on the basis of fatty acids.

The compounds of conjugated fatty acids obtained by the method according to the invention or mixtures containing these derivatives are valuable technical products which can be used in many ways. For instance their heat polymerisation takes place at a very fast rate, and therefore, the products can be converted into light colored polymer compounds under mild condition. They are also suitable for making raw material for lacquers, for example, alkyd resins or maleinate resins, for the preparation of plasticisers for the plastic industry and for many other purposes.

The invention is illustrated by, but is not intended to be limited to, the following detailed examples showing various embodiments of the invention. The proportions indicated are given by weight unless it is stated otherwise.

**EXAMPLE 1** 5,000 g of the distilled methyl ester of soya bean fatty acids containing 6.3% linolenic acid and 46.0% linoleic acid, combined as esters, were heated to a temperature of 120°C and mixed with 50 g of dried potassium methylate. The mixture soon turned into a brownish colour and was allowed to stand for a period of 5 hours being agitated from time to time. At certain time intervals several samples were taken and, after the catalyst had been removed by washing, they were used for spectrophotometrical determination of conjugated polyethenoid acids. The results are shown in the following table:

Reaction time in minutes	% isomerisation of triethenoid esters	% isomerisation of diethenoid esters
15	5	6
45	28	28
90	63	53
135	81	66
180	95	80
240	98	90
300	95	97

The results show that about 97% of the total ester of unconjugated polyethenoid acids is converted into the ester of the conjugated polyethenoid acids. Allowing for the margin of error of spectrophotometrical methods the isomerisation may be considered as practically complete.

Within a range of temperature between 100 and 140°C parallel experiments with the same material and the same catalyst gave corresponding results. At a temperature of 80°C the reaction is considerably slower, and at a temperature of 60°C only a very slow reaction rate was observed. The isomerisation is also slowed down if the amount of catalyst

decreases, and is hardly noticeable with an amount of 0.1% potassium methylate. An increase of the amount of the catalyst above 1% does not accelerate the reaction noticeably.

Analogous results were also obtained with thyl, propyl and butyl esters of soya bean acids; in addition, potassium ethylate, propylate and butylate instead of potassium methylate gave the same results.

**EXAMPLE 2** A distilled methyl ester of soya bean oil acids having the same composition as described in Example 1 was used as substrate. The catalyst was prepared by grinding potassium methylate with different alcohols in a molar ratio of 1 mole of potassium methylate to 0.5 - 2 moles of methyl alcohol, ethyl alcohol, normal or isopropyl alcohol or normal or secondary butyl alcohol respectively. In this way solid or semi-solid compositions were formed which were added to the mixture heated up to the necessary reaction temperature and the catalyst was quickly and uniformly distributed by agitation.

The following run may be taken as an example. 5,000 g of the methyl ester of soya bean fatty acids were reacted at a temperature of 140°C. The catalyst consisted of 50 g of potassium methylate and 53 g of secondary butyl alcohol. The run was made as described in Example 1. The progress of the isomerisation is shown by the results of the following table:

Reaction time in minutes	% isomerisation of triethenoid esters	% isomerisation of diethenoid esters
15	91	68
45	100	90
90	100	100
135	100	100
180	100	100

After a period of 45 minutes the isomerisation of the ester of linolenic acid was already complete, while after a period of 90 minutes the ester of the linoleic acid was completely isomerised. Compared with the run described in Example 1 the reaction time had been decreased to less than one third.

This run also shows that the range of temperature between 100 and 140°C is most favourable for isomerisation. The optimal composition of the catalyst is between a molar ratio of 1 mole of potassium methylate to 1 - 2 moles of alcohol where ethyl alcohol, propyl alcohol or butyl alcohol is used, while for methyl alcohol the best ratio is 1 : 1.5 - 2. Here, the optimum concentration of the catalyst was also 0.5 to 1% of potassium methylate.

**EXAMPLE 3** 3,000 g of distilled propyl ester of cotton seed fatty acids containing 45.5% linoleic acid combined as ester, were heated to a temperature of 140°C and mixed with a catalyst composition with stirring; the catalyst was obtained from 15 g potassium methylate and 22 g of isopropyl alcohol. When the reaction temperature was maintained at such a level with occasional stirring, the isomerisation was 85% complete after a period of 15 minutes; after a period of 45 minutes an isomerisation of 98% had taken place; after a period of 90 minutes an isomerisation of 100% was obtained.

After cooling of the reaction mixture and removal of the catalyst by washing with hot water an extremely light coloured product was obtained, as it was in the Examples 1 and 2.

**EXAMPLE 4** With mixtures of esters containing large amounts of linolenic acid and small amounts of linoleic acids a superimposition of isomerisation reactions of the esters of linolenic and linoleic acid was observed. The rate of isomerisation of the triply unsaturated acid is substantially larger than the corresponding rate of the doubly unsaturated acid. However, during the further reaction the content of conjugated tri-ethenoid acid is reduced, while the content of conjugated di-ethenoid acid exceeds the value calculated from the content of linoleic acid. The reason for this is, on the one hand, that the isomerisation of linolenic acid occurs in two steps whereby a conjugated di-ethenoid acid is formed during the first step, while the conjugated tri-ethenoid acid is formed only during the second step. On the other hand, the ester of the conjugated tri-ethenoid acid undergoes a further change during treatment whereby a cyclic di-ethenoid acid ester is formed. This will be illustrated by the following typical example.

5,000 g of distilled methyl ester of linseed oil acids containing 43.8% of linolenic acid and 14.3% of linoleic acid, combined as esters were heated to a temperature of 120°C and mixed with stirring with a catalyst prepared from 50 g of potassium methylate and 43 g of isopropyl alcohol. The mixture immediately turned a dark brown colour and was maintained at a temperature of 120°C with occasional stirring. Samples were taken periodically and the content of the several conjugated acids was determined spectrophotometrically. The results are given in the following table.

Reaction time in minutes	% isomerisation of triethenoid esters	% isomerisation of diethenoid esters
15	88	70
30	97	75
45	93	80
90	90	90
135	88	100

After a reaction period of 30 minutes the linolenic acid is completely isomerised while isomerisation of linoleic acid requires more time. If it is desired to obtain products containing a large amount of conjugated tri-ethenoid acids, the treatment is discontinued after a suitable period, in the above example, after 30 minutes. The run was repeated under the same conditions for a period of only 30 minutes and an extremely light coloured product was obtained containing 53.0% of conjugated fatty acids, which corresponds to a total isomerisation of about 92%.

By changing the temperatures and concentration of the catalyst it is easy to obtain a total isomerisation of almost 100%. For this purpose a temperature of 120°C is best, and the amount of catalyst may be twice as much as in the run described above. Under these conditions a product was obtained after a period of 1½ hours in which the unconjugated poly-ethenoid fatty acids were converted into conjugated acids up to an extent of 98%.

**EXAMPLE 5** 3,000 g of the methyl ester of linseed oil fatty acids were heated in a three necked reaction flask having a capacity of 5,000 ml and equipped with a stirrer, condenser, thermometer, gas inlet tube and gas outlet tube. The ester was heated up to a temperature of 120°C under a nitrogen blanket. Whilst continuously stirring and introducing nitrogen at a low rate 200 ml of a 14% solution of potassium tertiary butylate in tertiary butanol were added within a period of 10 minutes during which tertiary butanol and

some methyl alcohol was distilled off. The mixture was maintained under these conditions at a temperature of 120°C for 3 hours after which the mixture was cooled and washed several times with water and dried under vacuum.

To measure the extent of the isomerisation obtained, samples of the material were tested spectrophotometrically before and after isomerisation with respect to the content of unconjugated and conjugated fatty acids, giving the following results:-

	before	after	after further
	isomerisation		analytical
			isomerisation
% linoleic acid	16.4	-	-
% linolenic acid	43.9	-	-
% total unconjugated polyethenoid acids	60.3	-	-
% isomerised di-ethenoid acids	-	15.2	15.0
% isomerised tri-ethenoid acids	-	42.6	42.3
% total isomerised polyethenoid acids	-	57.8	57.3

Allowing for the fact that up to 10% tertiary butyl ester is obtained by this method, a practically complete isomerisation of the untreated material is achieved, which is confirmed by the further analytical isomerisation and measurements of the treated product.

**EXAMPLE 6.** 1,000 g of the methyl ester of soya bean fatty acids, 350 ml of n-heptane and 310 ml of tertiary butyl alcohol were heated to boiling in a glass flask of 2,000 ml capacity being equipped with an inserted thermometer, a rectification column having 12 theoretical plates and a condenser. Then 50 ml of a 5% solution of potassium tertiary butylate in tertiary butanol were added and heated under complete reflux conditions for a period of 2 hours. The content of the flask was at a temperature between 105 and 110°C. As soon as the distillate began to separate into two phases the alcoholic phase was continuously removed and the heptane phase was returned to the rectification column. During this treatment several samples of the content of the still were taken at certain time intervals in order to analyse their content of conjugated and unconjugated fatty acids and also the amount of tertiary butyl ester. The time of the treatment and the analytical results are shown in the following table:-

time of treatment (hours)	0	6	12	20	30
Tertiary butyl ester (% by weight)	-	42	58	79	99.5
isomerised diethenoid acid %	0.1	37.2	41.5	49.5	48.7
isomerised triethenoid acid %	0	8.0	7.6	7.2	7.0

While the starting material contained 55.7% of linoleic acid and 8% of linolenic acid, combined as ester, the further analytical isomerisation and the corresponding spectrophotometrical test of the completely esterified product gave a content of 48.3% of isomerised di-ethenoid fatty acids and 6.8% of isomerised tri-ethenoid fatty acids. Taking into account the difference between the molecular weight of the methyl ester used and the butyl ester obtained, a practically complete isomerisation of the unconjugated polyethenoid acid is obtained. This was achieved after a treatment of about 20 hours, namely before the

methyl ester used had been quantitatively converted into the corresponding tertiary butyl ester.

**EXAMPLE 7** By using the apparatus as described in Example 5, 2,800 g of distilled methyl ester of fish oil fatty acids were heated to a temperature of 140°C to which 300 ml of a hot 5% solution of caesium tertiary butylate in tertiary butanol were added. After having distilled the bulk of the tertiary butanol in a stream of nitrogen, the mixture was stirred under vacuum at the temperature of 140°C for two further hours, so that the complete time of treatment was two and a half hours.

Samples were taken from the mixture at intervals of 30 minutes and were measured spectrophotometrically. The results are shown in the following table:

	after 30 minutes	after 60 minutes	after 90 minutes	after 120 minutes	further analytical isomeri- sation
E 1 % 1 cm					
at 375 m $\mu$ (conjugated hexa ethenoid acid)	1.06	1.14	1.27	1.33	7.97
E 1 % 1 cm					
at 346 m $\mu$ (conjugated penta ethenoid acid)	5.11	4.95	6.49	6.18	37.17
E 1 % 1 cm					
at 315 m $\mu$ (conjugated tetra ethenoid acid)	34.80	35.50	39.56	35.98	80.53
E 1 % 1 cm					
at 268 m $\mu$ (conjugated triethenoid acid)	165.96	166.03	163.89	143.49	112.83
E 1 % 1 cm					
at 233 m $\mu$ (conjugated diethenoid acid)	163.83	163.36	165.49	150.11	113.0

It is evident that the isomerisation leads to a substantially complete conversion of the unconjugated polyethenoid acids to acids containing conjugated systems. After 30 minutes the isomerisation is practically complete. This example shows furthermore, that the isomerisation could also be carried out partially, i.e. unconjugated polyethenoid acids having 3 or more double bonds may be converted into the corresponding conjugated diethenoid acids of tri-ethenoid acids.

**EXAMPLE 8.** 3600 g of the methyl ester of soya bean fatty acids were heated together with 180 g of ethylene diamine to a temperature of 140-160°C for a period of four hours, after which the methyl alcohol liberated was removed under vacuum. The mixture partially converted into the diamides contained 6.3 % linolenic acid and 49.4%



linoic acid in the combined form. After heating to a temperature of  $120^{\circ}\text{C}$  10 g of potassium methylate were added with stirring and the mixture was left at this temperature for one hour. The catalyst was removed by adding 50 g of Fuller's earth followed by filtration. The light colored product thus obtained contained 6.3% isomerised tri-ethenoid acid and 49.1% isomerised di-ethenoid acid, corresponding to a total isomerisation of nearly 100%.

In this run the amount of ethylene diamine used was equivalent to the content of polyethenoid fatty acid. This shows that the amides of unconjugated polyethenoid acids are completely isomerised with small amounts of catalysts within a relatively short time.

The claims defining the invention are as follows:

1. A process for the catalytic isomerisation to conjugated polyethenoid compounds of monohydric alcohol esters, amides and polyamides of unconjugated polyethenoid acids, characterised in that the unconjugated polyethenoid acid compound is treated with catalytic amounts of 0.05 to 5.0% by weight of alkali metal alcoholate at a temperature between  $60$  and  $180^{\circ}\text{C}$ , in the absence of compounds which will react with the alkali metal alcoholate to inactivate it and in particular water, free fatty acids or peroxides. (31st May, 1961).
2. A process in accordance with claim 1 wherein the unconjugated polyethenoid acid compound is treated with 0.3 to 2.0% by weight of alkali metal alcoholate. (31st May, 1961).
3. A process in accordance with claim 1 or claim 2 wherein the alkali metal alcoholate is the alcoholate of a monohydric alcohol. (31st May, 1961).
4. A process according to any preceding claim wherein the treatment is carried out between  $100$ - $140^{\circ}\text{C}$ . (31st May, 1961).
5. A process in accordance with any preceding claim wherein mixtures of monohydric alcohol esters, amides and polyamides of the unconjugated polyethenoid acids or fatty mixtures containing these compounds are used as starting material. (31st May, 1961).
6. A process in accordance with any preceding claim characterised in that mixtures of alkali metal alcoholates with monohydric alcohol in a proportion of one mole of alkali metal alcoholate per 0.1 to 5.0 moles of alcohol or solutions of the alkali metal alcoholates in the said alcohol are used as catalyst. (31st May, 1961).
7. A process in accordance with claim 6 wherein the proportion of alkali metal alcoholate to alcohol is 1 mole to 0.5 to 2.0 moles. (31st May, 1961).
8. A process in accordance with any preceding claim characterised in that the catalyst is formed from alkali metals, alkali metal hydrides or organic alkali metal compounds reacting with alcohol present in the reaction mixture to give the corresponding alkali metal alcoholate. (31st May, 1961).

9. A process in accordance with any preceding claims wherein the reactants contain a monohydric alc hol. (31st May, 1961).
10. A process in accordance with any preceding claim characterised in that potassium, rubidium and/or caesium alcoholates as such or in admixture with alcohols are used as catalyst. (31st May, 1961).
11. A process in accordance with any preceding claim characterised in that the reaction is carried out in the presence of polar or non-polar solvents which are inert with respect to the catalyst. (31st May, 1961).
12. A process in accordance with claim 11 wherein the solvent used is selected from heptane, dimethyl formamide or dimethyl sulphoxide. (31st May, 1961).
13. A process in accordance with any preceding claim wherein isomerisation of unconjugated polyethenoid acid esters is carried out so that interesterification takes place at the same time. (31st May, 1961).
14. A process in accordance with any preceding claim wherein isomerisation of unconjugated polyethenoid acid esters is carried out in the presence of an amine so that aminolysis takes place at the same time. (31st May, 1961).
15. A process in accordance with any preceding claim characterised in that volatile compounds used as solvents are removed by distillation during the isomerisation. (31st May, 1961).
16. A process for the isomerisation of compounds of unconjugated polyethenoid acids with catalytic quantities of alkali metal alcoholates substantially as described with reference to the foregoing Examples. (31st May, 1961).
17. Compounds of conjugated polyethenoid acids wherever obtained by any of the processes claimed in claims 1 to 16. (31st May, 1961).

PHILLIPS, ORMONDE, LE PLASTRIER & KELSON.

Patent Attorneys for Applicant.

\*\*\*\*\*

Related Art:

Serial No.

Application No.

Classification.

118, 542

5784/42

09. 2; 79. 3; 09. 1

144, 603

17, 907/48

09. 1; 09. 3.

Printed for the Government of the Commonwealth by  
A. J. Arthur, Commonwealth Government Printer, Canberra.